

Final Report for AOARD Grant AOARD-10-4155 "Carbon-coated current collectors for high-power Li-ion secondary batteries"

2011.9/20

Name of Principal Investigators:

- e-mail address : nlw001@ntu.edu.tw
- Institution : National Taiwan university
- Mailing Address : 1, sec. 4, Roosevelt Rd, Taipei 106, Taiwan
- Phone : +886-2-23627158
- Fax : +886-2-23623040

Period of Performance: 20/09/2010 – 19/10/2011

Abstract: The ultimate goal of this project is to develop a viable C-coating process of the current collector in order to improve the overall power performance of the electrode of Li-ion batteries. Two major parts of research works toward this goal have been carried out during this period of performance. Firstly, Al and Cu foils have been subjected to high-temperature thermal chemical vapor deposition (T-CVD) to produce surface C-coating, and the resulting foils have been used as the current collectors for LiFePO_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It was found that the C-coating has remarkably enhance the power performance of the both electrodes. It has been shown by surface and electrochemical analyses that the enhancement the enhancement can be attributed to the combination of two factors, including removal of the native oxide layer and modification of surface hydrophobicity, which improves adhesion of active layer, on the current collector surface. Both contribute to the reduction of the resistance at the current-collector/ active layer interface. Secondly, a low-temperature plasma-assisted chemical vapor deposition (PA-CVD) vacuum chamber has been setup and tested. The design of the chamber allows for roll-to-roll plasma treatment of metal foils under vacuum condition, and it is ready for carry out the low-temperature coating process in the next-year phase of research.

Introduction:

The basic principle for achieving high-power capability of a battery is minimizing the overall resistance of the electrochemical system. For Li-ion batteries, much research effort has been devoted in the past to minimize the ionic diffusion resistances and electronic resistance associated with the electrode active materials. In the typical electrode configuration, the layer containing the active material is supported on a metallic current collector. The interface between the current collector and active layer imposes additional resistance to charge transfer within the electrode. This resistance source has not received sufficient attention in the past, presumably because it was not considered of significance for the low-power Li-ion electrode materials. However, the advancement in the material synthesis technologies has reduced the ionic and electronic resistances associated with the active materials to certain point that they become competitive to the other resistance sources. Thus, the significance of the electronic resistance at the active layer/current collector (AL/CC) interface is worthy of careful re-examination.

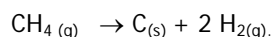
The objects of this study is to prepare C-coated Al current collectors by two different coating processes, including high-temperature thermal chemical vapor deposition (T-CVD) and low-temperature plasma-assisted chemical vapor deposition (PA-CVD), and to characterize their electrochemical properties pertain to the power performance and cycling stability of Li-ion batteries. At least two beneficial effects are anticipated to result from the C-coating. For one, the C-coating removes the native surface oxide layer on the metal current collectors. For the other, the C-layer is hydrophobic in nature and hence helps to

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 30 SEP 2011		2. REPORT TYPE Final		3. DATES COVERED 20-09-2010 to 23-09-2011	
4. TITLE AND SUBTITLE Carbon-Coated Current Collectors for High-Power Lithium Ion Secondary Batteries				5a. CONTRACT NUMBER FA23861014155	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Nae-Lih Wu				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Taiwan University, Department of Chemical Engineering, Taipei, 106, Taiwan, NA, NA				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD, UNIT 45002, APO, AP, 96338-5002				10. SPONSOR/MONITOR'S ACRONYM(S) AOARD	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-104155	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The goal of this project is to develop a viable C-coating process of the current collector in order to improve the overall power performance of the electrode of Li-ion batteries. Two major parts of research works toward this goal were carried out. (1) Al and Cu foils were subjected to high-temperature chemical vapor deposition (T-CVD) to produce surface C-coating, and the resulting foils were used as current collectors for LiFePO4 and Li4Ti5O12. The C-coating remarkably enhanced the power performance of both electrodes. The enhancement was attributed to a combination of two factors--removal of the native oxide layer and modification of surface hydrophobicity--both of which reduced the resistance at the current-collector/ active layer interface. (2) A low-temperature plasma-assisted chemical vapor deposition (PA-CVD) vacuum chamber was built and tested. The design of the chamber allows for roll-to-roll plasma treatment of metal foils under vacuum condition, and it is ready for carry out low-temperature coating processes in the next-year phase of research.					
15. SUBJECT TERMS lithium ion secondary battery, Carbon-Coated Current Collectors, Chemical Vapro Deposition					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

improve the interfacial bonding. Both effects are expected to reduce the AL/CC interfacial resistance. The ultimate goal is to develop a viable C-coating process of the current collector in order to improve the overall power performance of the electrode of Li-ion batteries.

Experiment:

In a typical T-CVD process, a current collector, either Al or Cu, with a dimension ranging from 4cm x 10cm to 10 cm x 10 cm is placed inside a horizontal hot-wall reactor, and CH₄ is allowed to flow over the foil surface. The etched Al foil is a commercial product processed with a proprietary technique, courtesy of Japan Capacitor Industrial Co., Ltd., while Cu is from Furukawa Electric Co., Ltd. The coating process was carried out at 600 °C for a period time ranging from 2 to 20 hours. The C coating is formed through thermal cracking of CH₄, i.e.,



The morphologies of the materials and electrodes were characterized by scanning electron microscopy (SEM; LEO1530). The surface area and pore structures of the C fibers were determined by N₂ adsorption (Micromeritics; ASAP2010). The X-ray photoelectron spectroscopy (XPS) analysis employed an Al K α X-ray source operated at 15 kV and 100 W, and used a beam size of 400 μm and a pass energy of 20 eV for spectrum acquisition. Sputtering gun was operated at 3 kV and 1 μA with a sputtering area of 2 mm x 2 mm.

Two types of active electrode materials have been used for test, and they are LiFePO₄ (LFPO) and Li₄Ti₅O₁₂ (LTO) as cathode and anode material, respectively. The former was purchased from Photech (d_{50} = 3.0 μm), while the latter from BTR Energy Material (d_{50} = 100 nm). They both were used as received.

The LFPO active layer contains 85 wt.% LFPO powder, along with carbon conducting additives and polymeric binder (Polyvinylidene difluoride; Aldrich). The electrodes were roll-pressed and finally dried at 120 °C for 6 hr in vacuum. The resulting LFPO electrodes have a weight of ca. 2.50 mg/cm². The LTO electrode contains 80 wt.% LTO powder with a mass of ca. 2.83 mg cm⁻². Both electrodes were assembled together with Li-foil counter electrodes to make CR2032 coin cells, and the electrolyte was 1 M LiPF₆ in a 1:2 v/v mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC; Mitsubishi Chemical). All the cells were assembled in a dry room where the dew point was maintained at between -40 and -45 °C.

Electrochemical characterizations include constant current charge/discharge (C/D) test and electrochemical impedance spectroscopy (EIS). The C/D tests were carried out with selected current rates on a battery tester (Arbin, model: MCN6410). The charge and discharge phases of a cycle were always conducted at the same selected current rate. EIS analysis (AUTOLAB, Eco Chemie PGSTAT30) was conducted with the frequency ranging from 10 mHz to 60 kHz and a voltage amplitude of 10 mV at the open-circuit voltage of a cell (OCV).

Results and Discussion:

1. LiFePO₄ on Al:

In our previous published work [1] it has been shown that the use of T-CVD derived C-coated etched Al current collector can greatly improve the high-rate performance of the electrode. The C-coating process was carried out for 20 hrs. One of the objects of this study is to evaluate the effect of coating thickness, which is a function of depositing period, on the performance of the LFPO electrode.

Etched Al current collectors have been subjected to T-CVD process for 1, 5 10 and 20 hrs, and Fig. 1 plots the Secondary ion mass spectroscopy (SIMS) C spectra showing the C

signal as function of sputtered depth. As shown, the the C thickness increases with increasing treatment length. After 10 hrs of treatment, there is already a plateau of constant C intensity of ca. 25 nm. On the other hand, after 20 hrs of treatment, the thickness extends to greater than 100 nm. A peak occurs at ca. 80 nm, which is likely due to presence of the Al-carbide phase.

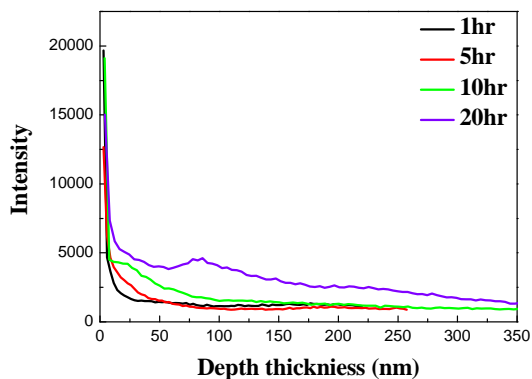


Figure 1. SIMS C spectra acquired from C-coated Al current collector for different period of times ranging from 1 to 20 hours.

Figure 2 shows the performance of the LFPO electrodes using these current collectors. First, the capacity of each electrode decreases with increasing current rate. Secondly, under the high C rate, for example 10C, the capacity increases with increasing C-deposition time until 10 hrs, above that there is no further improvement. Figure 3 a~c shows the charge/discharge curves corresponding to these data points.

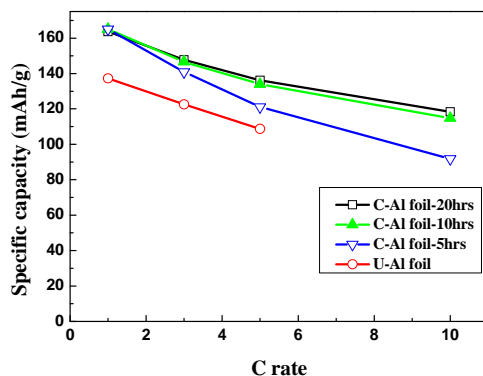


Figure 2: Specific capacity versus C-rate for LFPO electrodes using Al current collectors which have been subjected to T-CVD for different period of time.

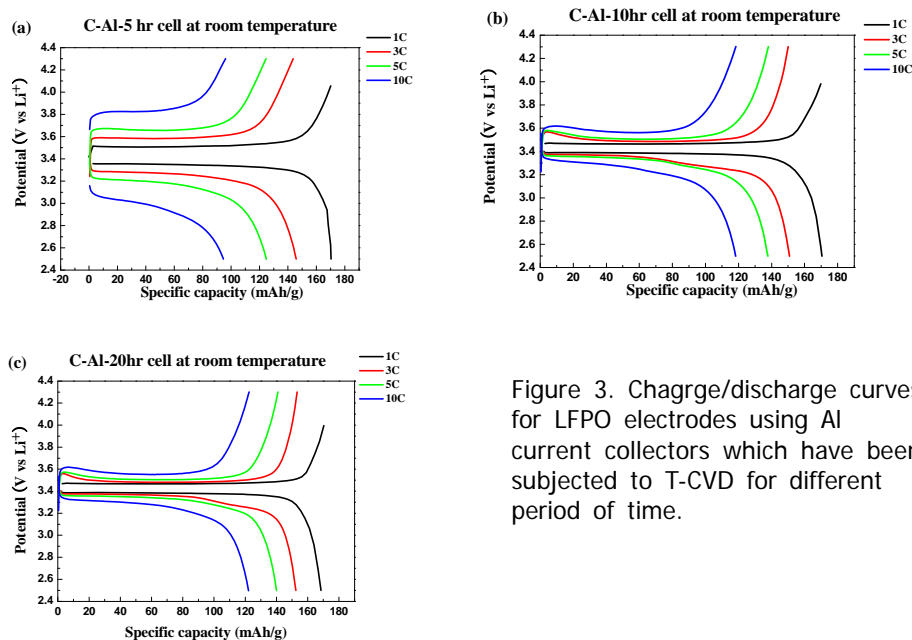


Figure 3. Charge/discharge curves for LFPO electrodes using Al current collectors which have been subjected to T-CVD for different period of time.

2. LTO on Al and Cu

The Al foil has a smooth surface except for some mechanical scratches. Figures 3a~d show the surface morphologies of E-Al, C-E-Al, Cu and C-Cu current collectors, which have more profound surface features. E-Al foil has a porous surface structure showing circular pores overlapping with one another to form void opening of $\sim 1 \mu\text{m}$ at surface (Fig. 3a). After the high-temperature C-coating process, the porous structure remains (Fig. 3b), while the interior surface is coated with a conformal C layer. The surface chemical compositions of the Al-based current collectors have been characterized in detail in a previous study [1] by using X-ray photoelectron spectroscopy (XPS). In brief, both the Al and E-Al current collector possesses a native oxide surface layer with decreasing oxygen content with depth. The C-E-Al current collector has a composite surface layer that consists of a top C layer and a bottom Al_4C_3 layer. The C-coating thickness is greater than $\sim 70 \text{ nm}$, varying from one location to another. The original surface oxide layer has been broken into debris dispersed within the C layer.

The Cu current collector possesses a rough surface structure that shows large particles of $1\sim 3 \mu\text{m}$ in diameter with smaller particles of ca. $20\sim 30 \text{ nm}$ at their surfaces (Fig 3c). After the T- CVD process, the foil surface is covered with a conformal C layer (Fig. 3d). The XPS data confirm that the C-Cu current collector has a higher C content on surface than the Cu current collector, while the latter has a higher oxygen content. The thickness of the carbon layer on C-Cu is ca. 45 nm , according to the secondary ion mass spectroscopy (SIMS) analysis.

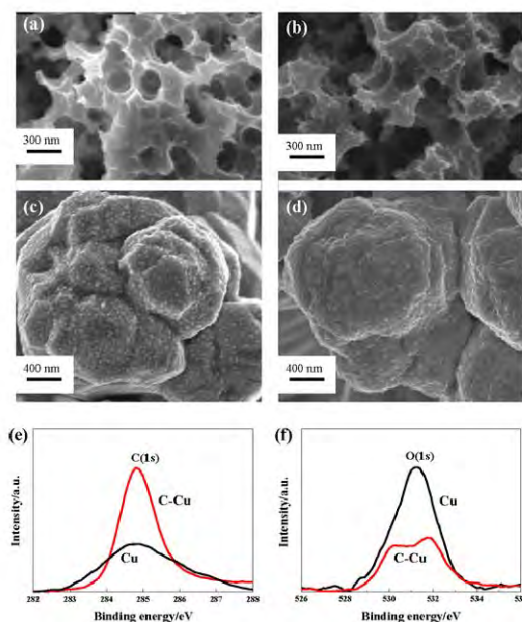


Figure 3. Material characterizations. (a)~(d) are SEM micrographs of E-Al (a), C-E-Al (b), Cu (c) and C-Cu current collectors. (e)~(f) show the XPS C(1s) and O(1s) spectra for the Cu and C-Cu current collectors.

Figure 4a plots the capacity data under different C-rates for the five different electrodes. 25 cycles have been conducted under every selected current rate and the average values are summarized in Fig. 4b. Selected discharge voltage curves (under 3C rate) are shown in Fig. 4c. For brevity, the coin-cells will be referred to with the same notation as the electrodes they contain. As shown, the Al cell shows the lowest capacities for all the adopted current rates. Using the etched Al foil (the E-Al cell), which gives a higher CC/AL interfacial area than smooth Al, results in slight increase in capacities below 5C rate. The C-E-Al cell shows remarkable capacity improvement under all current rates, and the improvement is particularly strong under high current rate. Compared with the Al cell, the capacity has been increased by 20 % and 150 % under 1 C and 20 C rates, respectively.

The Cu cell exhibits higher capacities than the Al and E-Al cells at all current rates and performs closely to the C-E-Al cell. C-coating on the Cu surface further markedly enhances the capacity. Overall, the power performance of these cells is in the order of $\text{Al} < \text{E-Al} < \text{Cu} \sim \text{C-E-Al} < \text{C-Cu}$. For achieving a capacity of 130 mAh g^{-1} , the current rate has been increased from 1 C for the Al cell to 5 C for C-E-Al and to 7 C for C-Cu.

It is also worth noting that after cycling 150 cycles under various high rates as shown in Fig. 4a, the cells show essentially no fading. This reflects the cycling stability nature of the active material.

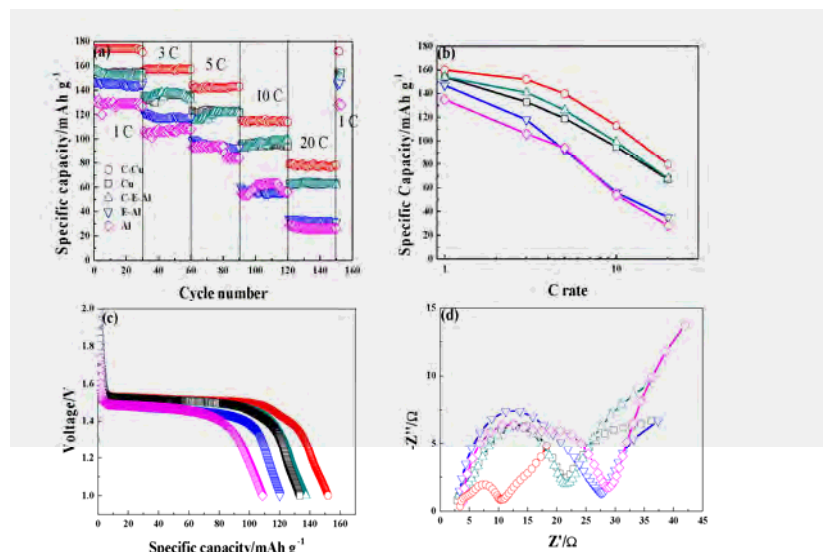


Figure 4. Electrochemical characterizations. (a) Capacity data vs. cycle number; (b) capacity data vs. current rate; (c) Discharge voltage curves (3C rate); and (d) Nyquist plots for cells using different current collectors (○: C-Cu; □: Cu; △: C-E-Al; ▽: E-Al; ◇: Al).

For all these cells, their Nyquist plots show a distorted semi-circle above ca. 20 Hz (Fig. 4d). Theoretically, any interface that can be described by a parallel RC equivalent circuit unit will give a semi-circle in the Nyquist plot. The semi-circle over this frequency range for a Li-ion battery electrode has typically been attributed to the impedance associated with the electrode/electrolyte interface, and the width of the semi-circle along the real-part (Z') axis to the charge-transfer resistance. However, in studying the C-based electric double-layer capacitor (EDLC), Portet et al. [2] showed that the use of Al current collector, which has a native surface oxide layer, gave rise to a semi-circle above ca. 80 Hz, while the use of C-coated Al current collector did not. This has also been confirmed in our previous study on another C-coated Al current collector [3]. As EDLC does not involve charge transfer across the electrode/electrolyte interface, the semi-circle seen on the Al current collector must originate from the CC/AL interface, and the associated capacitor element of the RC unit arises from the thin oxide layer as well as patches of thin electrolyte film between the active layer and the current collector due to poor adhesion. Therefore, it is believed that the semi-circles shown in Fig. 4d include both the charge-transfer and CC/AL interfacial impedances, and the width of these semi-circles are the sum of the charge-transfer and CC/AL interfacial resistances. Since all the electrodes studied here have the same active material and electrolyte, one expects the same electrochemical behaviors at the solid/electrolyte interface. Therefore, the differences shown in their semi-circle resistances are caused primarily by the different resistances at the CC/AL interface. Accordingly, it can be concluded that the CC/AL interfacial resistance follows the order of $\text{Al} > \text{E-Al} > \text{Cu} \sim \text{C-E-Al} > \text{C-Cu}$, which is exactly the reverse order of their capacities.

The reduction of the CC/AL interfacial resistance by the C coating may be understood in terms of the surface chemistry of the current collector. The presence of insulating oxide layers at the pristine Al and Cu current collectors would impose significant resistance to current flow across the CC/AL interface. Furthermore, the oxide surface is hydrophilic, while the coating slurry and dried active layer are both hydrophobic in nature. The different polarities would result in poor film adhesion and hence high interfacial resistance. Replacing the surface oxide layer with the C layer can significantly reduce these problems. Firstly, it directly reduces the surface resistance by destroying the native oxide layer. Secondly, it can

turn the current-collector surface from being hydrophilic to hydrophobic, and hence improve the adhesion of the active layer. To demonstrate such a property change, Table 1 compares the contact angle data of water on these current collectors. The higher the contact angle, the greater is the surface hydrophobicity. As shown, after the CVD C deposition treatment, the surfaces of both Al and Cu current collectors exhibit very significant increase in hydrophobicity.

Table 1. Contact angles of water on current collectors

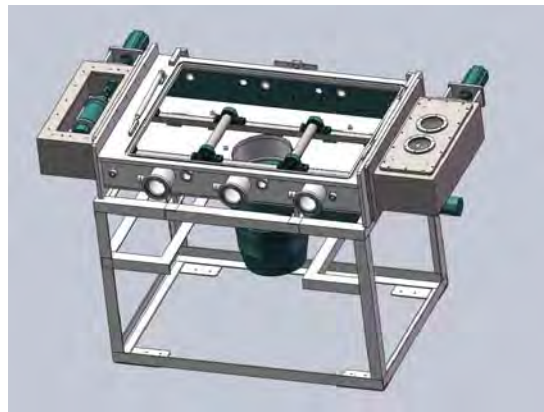
Type of current collector	Contact angle
Al	74°
E-Al	87°
C-E-Al ^a	116°
Cu	102°
C-Cu ^a	129°

a: C-coating is produced at 600 °C in CH₄ for 20 hrs.

3. PA-CVD setup

In order to carry out PA-CVD, a special designed vacuum chamber that allow for moving of the current collector during the CVD process without breaking vacuum is set up. As shown in Fig. 5a, the vacuum chamber is equipped with two rollers respectively on two sides of the chamber. In operation, a roll of current collector, either Al or Cu, will be loaded to one of the rollers and the foil will be extended to pass through the chamber and then to the other roller. The rolling speed is driven by a step-motor that is controlled by a computer for adjusting its speed. Once the current collector is at position, the top of the chamber will be sealed with three plates that contains at maximum different kinds of plasma guns (Fig. 5b, c). At its bottom, the chamber is attached to a turbo-pump for evacuation. Reactive gas is allowed to flow into the chamber with a mass flow meter for flow-rate control.

For preliminary test of the system, the roller is loaded with Al current collector, and this current collector acts only as a conveying belt. The working piece of the current collector foil, typically 4cm x 10 cm, will be attached onto this belt and moved horizontally and treated under selected conditions. Upon completion, the working piece is removed from the belt, and new foil will be attached again for the next example. This system is now in full operation after initial test runs, and it will be used during the next phase of this project.



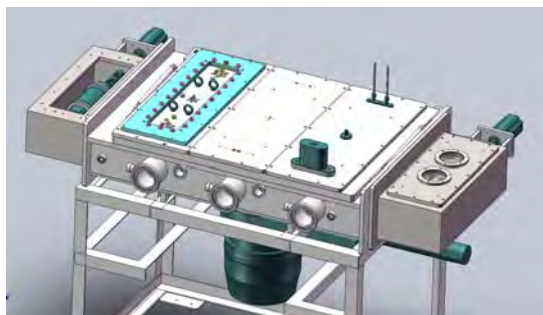


Figure 5. Schematics of the PA-CVD system.

List of Publications:

Publication:

Hsien-Chang Wu, Eric Lee, Nae-Lih Wu*, and T. Richard Jow, "Effects of Current Collectors on Power Performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode for Li-Ion Battery," J. Power Sources, in press (2011).

Presentation:

The 219th Electrochemical Society meeting, "High Power $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode Employing Cu Current-Collectors with Conformal Carbon Coating," May 1-6, 2011, Montreal, QC, Canada